SCIENCE FOR GLASS PRODUCTION

SPECTROPHOTOMETRIC DETERMINATION OF THE REDOX STATE OF GLASS

S. V. Mulevanov[1, 2] and V. M. Nartsev[1]

The main difficulties of making an accurate determination of the redox state of glass are noted. The specific effect of tin on the valence equilibrium of iron in the surface layers of float-glass is shown. The spectrophotometric method of determining heterovalent forms of iron in commercial silicate glasses, which is applicable for flat and hollow articles, is described. The method is distinguished by high speed and accessibility.

Key words: commercial silicate glass, redox state of glass, optical spectrophotometry, valence equilibrium of iron, calibration curves, phenanthroline method, tin and iron 'hump'.

Iron is an unavoidable component of all industrial silicate glasses. It enters the glass from the main raw materials during the preparation and transport of batch (hardware iron) as well as from refractories of the glassmaking furnace during melting. In some cases it is introduced intentionally, usually in the form of crocus or iron chromite. Two heterovalent forms of iron — Fe^{2+} (ferrous, or reduced, form) and Fe^{3+} (ferric, or oxidized, form) coexist in any glass.

Ordinarily, the iron in glass is taken to mean 'total iron' — the content as a percent by weight in terms of Fe_2O_3. Even though the total iron content in commercial silicate glass is low (0.05 – 0.1% in transparent float glass up to 0.3 – 0.5% in architectural bronze or grey glass and up to 0.6 – 0.8% in container glass), it has a very large effect on the glassmaking process.

In silicate melt the bi- and trivalent forms of iron are in dynamic equilibrium, which is influenced by the presence of oxidizers and reducers in the batch, the composition of the gaseous atmosphere, the melting temperature, the total iron content and the basicity of the glass-forming matrix. The reducers increase the content of bivalent iron, and the melting temperature and total iron content have a similar effect. Increasing the basicity of the glassy matrix (i.e., depolymerization), specifically, the concentration of alkali oxides, results in oxidation of the iron. The substitution of alkaline-earth oxides for alkali oxides is accompanied by the reduction of iron, which is due to the valence-coordination transition $Fe^{3+}O_4 \rightarrow Fe^{2+}O_6$, as was shown in [1]. This displacement of the valence-coordination equilibrium could also be due to the introduction of P_2O_5 [2].

The current specifications for the quality of glass articles poses a number of problems concerning the reduction of total iron as well as stabilization of the redox state of the molten glass, the indicator of which is the concentration ratio Fe^{2+}/Fe^{3+}. This is done using the redox index, which is taken to mean the ratio of the mass content (% FeO) to the total content (% $Fe_2O_{3\ total}$):

$$\text{Redox} = FeO/Fe_2O_{3\ total}.$$

A change in the ratio between bi- and trivalent iron can be critical for light transmission, the color coordinates and purity, cordiness, rates of fusion and homogenization of the melt, as well as additional formation of bubbles [3]. This parameter can be used to control the glassmaking process — adjustment of the content of oxidizers and reducers in the batch, the composition of the gas atmosphere and the temperature regime [4].

It should be noted that the determination of the mass content (%) of Fe^{2+} and Fe^{3+} in glass by means of conventional chemical methods (national OST 21-67.3–91, OST 21-67.8–91 and other international standards) is a laborious

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[1] V. G. Shukhov Belgorod State Technological University (BGTU), Belgorod, Russia.

[2] E-mail: smulevanov@mail.ru.

and time-consuming process and requires a high skill level in performing the analytical operations. At the same time the use of optical spectrophotometry of glass makes it possible to attain high accuracy and speed, which is especially important for routine control of the glassmaking process. This method, in contrast to other physical spectral methods (atomic-emission spectroscopy [5], electron paramagnetic resonance and Mössbauer spectroscopy) is characterized by great simplicity and accessibility. X-ray fluorescence (XRF) analysis, which has been widely used in recent years, makes it possible to obtain adequate results for the content of total iron, but it is unsuitable for determining the heterovalent forms of iron because the emission lines of $Fe^{2+}K\alpha$ and $Fe^{3+}K\alpha$ overlap with one another. In principle such a determination can be made by analyzing the XR-emission $L\alpha$ spectrum of iron [6], which, however, is still not used in practice.

The determination of the heterovalent forms of iron in float glass merits special consideration. The problem consists of the fact that while the glass ribbon is present in the float tank the iron present in glass is subjected to reduction — the upper layers as a result of the action of hydrogen from the protective atmosphere and in part the tin vapor and the lower layers — metallic tin which transforms first into the bi- and then the trivalent form in the course of diffusion.

Depending on the thickness of the glass ribbon the penetration depth of tin into the bottom layer can reach $10 - 40 \mu m$ in the presence of a 'hump', i.e., a local maximum of the concentration at depth $4 - 10 \mu m$ [7]. The position of the 'tin hump' corresponds to the maximum concentration of Fe^{2+}, and an iron 'hump' corresponding to the highest concentration of Fe^{3+}, present at the position of a modifier, is observed at a depth of about $15 \mu m$ [8]. At large depths the Fe^{3+} concentration decreases and this iron transforms to tetrahedral coordination. Starting at a depth of about $30 \mu m$ the ratio between the bi- and trivalent iron stabilizes and approximately corresponds to this ratio in the glassmaking furnace.

The residual metallic time, having diffused into the bottom surface layer of the glass, plays the role of a reducer in the process of analytical operations and distorts the true results for the ferrous and ferric forms of iron. The effect of this factor is all the more significant, the longer the glass melt remains in the float tank (i.e., the thicker the glass ribbon) and the higher the temperature. Thus, the ratio of the heterovalent forms of iron is ultimately different from that in the glassmaking furnace. To obtain objective results for accurate determination of the redox index of the glass, which are important for controlling the glassmaking process, in our view, the surface layers should be removed to depth $0.1 - 0.2$ mm before the chemical analysis of the glass is performed.

Each ionic form of iron is associated with its own optical absorption spectrum. Trivalent iron has characteristic absorption peaks at 330 nm (corresponding to the absorption edge for float glass) and 380 nm (both in the UV region), making the glass opaque to UV radiation. These peaks presumably correspond to the absorption due to trivalent iron ions in tetrahedral coordination and imparting a yellow-brown color to the glass. A weaker, double peak is also observed in the range $410 - 440$ nm, presumably corresponding to the absorption due to trivalent iron, located in octahedral coordination and imparting a greenish-yellow color to the glass.

A wide, deep absorption band due to bivalent iron is observed at 1050 nm (IR range). The diffuseness and difference from the classical (Gaussian) shape give a basis for assuming that it is a co-evolution of several peaks corresponding to the absorption due to ions occupying octahedral positions with different degrees of distortion of symmetry [9]. This absorption imparts greenish – light-blue coloring to the glass, which is $15 - 20$ times more intense that the coloring due to trivalent iron. A superposition of absorption bands due to both ionic forms of iron is observed in the glass; in addition, the color of the glass is determined by the ionic balance.

In glass production the light transmission T is measured at the wavelength 550 nm, corresponding to the highest sensitivity of the human eye. This index T_{max} is close to the integral light transmission, but it is our view that a more precise characteristic can be obtained (without any special problems) by integrating the transmission spectrum in the entire visible range using the EXCEL software.

In practice a spectrophotometer can be used to obtain transmission spectra and the optical density indices. The spectrophotometric method of determining the heterovalent forms of iron is based on measurement of the transmission spectrum of glass and calculation of the absorption at wavelengths characteristic for Fe^{3+} and Fe^{2+} (about 380 and about 1100 nm, respectively) and on the determination of the concentrations of these ions (of the corresponding oxides) by means of calibration curves.

Until very recently the spectrophotometric method was used to determine the optical characteristics of sheet glass, but in principle it can be widely used in the production of different hollow articles (containers, medical and illumination engineering articles). A sample with the minimal dimensions of about 13×13 mm (for PÉ-6100UF, SF-56 spectrophotometers) can be used for the measurements. It is not necessary to obtain a polished plane-parallel plate, which requires appropriate equipment and considerable labor expenditures. The sample can be cut from the side surface of a hollow article.

The operation of the SF-56 spectrophotometer includes the use of the Sf56 control software (Analys for PÉ-6100UF) in the precision scan regime with a 1 nm step at wavelengths ranging from 350 to 1100 nm and slit width 1 nm (for a planar sample). If the sample is curved and its radius is shortened, an adjustment must be made for the operation of the spectrophotometer (increase of the slit width).

First, the spectrum of air is obtained until a reproducible line up to 100% transmission is obtained, indicating that the instrument is in a stationary regime. The glass sample must be well annealed without any visible defects (thickness differences, cords, bubbles, crystals or pronounced cold appear-
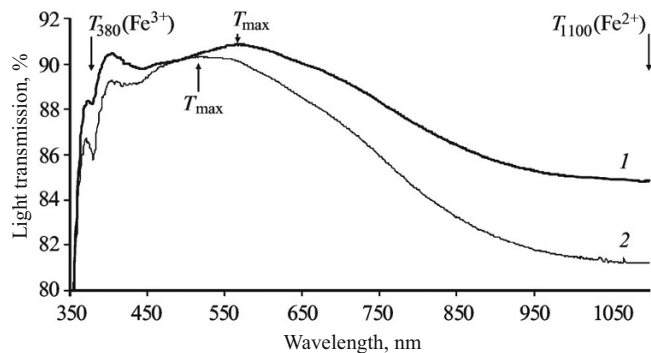
Fig. 1. Transmission spectrum of colorless container glass (*1*) and sheet float-glass (*2*).

ance of the surface) and carefully degreased. The spectrum obtained for the glass sample must not contain any optical distortions (artifacts) associated with unsatisfactory preparation or incorrect placement of the sample.

The transmission spectra of a colorless sample of container glass of thickness 3.12 mm with radius of curvature 40 mm and sheet float-glass of thickness 3.82 mm are presented in Fig. 1. The spectra were obtained in the regime presented above on an SF-56 spectrophotometer with slit width 6 and 1 nm, respectively.

The calculation of the concentrations of the heterovalent forms of iron includes the measurement of the thickness of the sample (*d*, cm) with a digital micrometer with accuracy ± 0.01 mm and the determination of the minimal values of the transmission near 380 nm (T_{380}) and 1100 nm (T_{1100}) as well as the transmission peak in the range $520 – 560$ nm (T_{max}).

The mass content ω (%) of total iron Fe_2O_3 and FeO is calculated from the relations

$$\omega(FeO) = \frac{D_1}{k_1}; \quad \omega(Fe_2O_3) = \frac{D_2}{k_2},$$

where k_1 and k_2 are the mass coefficients of absorption due to FeO and Fe_2O_3 (determined according to the calibration curves), $\%^{-1} \cdot cm^{-1}$; D_1 and D_2 are the optical densities referenced to the thickness of the glass sample taking account of the background, cm^{-1}.

The quantities D_1 and D_2 are calculated from the relations

$$D_1 = \frac{-\ln(T_{1100}) + \ln(T_{max})}{d};$$

$$D_2 = \frac{-\ln(T_{380}) + \ln(T_{max})}{d}.$$

To determine the mass coefficients of absorption for iron oxides it is necessary to construct calibration curves for glass samples for which the mass content of Fe_2O_3 and FeO is de-

termined by the methods of analytical chemistry [$\omega_{c.a}(Fe_2O_3)$, $\omega_{c.a}(FeO)$]. For this it is best to use the phenanthroline method, which is more accurate than the widely used sulfosalicylate method. The phenanthroline method can be used to obtain a deviation of the mass content of approximately 0.0002%, which corresponds to relative error $\leq 1\%$.

To determine the mass coefficients of absorption the experimental points are plotted in the coordinates $\omega_{c.a}(Fe_2O_3)$, $\% – D_2$, cm^{-1}, and $\omega_{c.a}(FeO)$, $\% – D_1$, cm^{-1}, to which straight lines are fit. The tangents of the slope angles of these straight lines correspond to the mass coefficients of absorption. It is not acceptable to use calibrations from the literature or obtained on other spectrophotometers because of the difference in the designs of these instruments.

In summary, data obtained by the conventional analytical method are still required in order to use the method proposed above. However, these data are needed only to construct the calibration curves and to make periodic adjustments. The spectrum itself is obtained in $3 – 4$ min, and all subsequent EXCEL calculations on a PC can take less than 1 min.

If chromophoric centers (sulfides, compounds of chromium and other elements) are present [10], the procedure proposed here can be adjusted taking account of the absorption due to these groups at the corresponding wavelengths. For opalescent and opacified illumination-engineering glasses the increase in absorption in the entire spectral range and the change in the shape of the spectrum in the short-wavelength region must be taken into account.

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